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Reconstruction of deglacial sea surface temperatures in the tropical Pacific from selective analysis of a fossil coral

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[1] The Sr/Ca of coral skeletons demonstrates potential as an indicator of sea surface temperatures (SSTs). However, the glacial-interglacial SST ranges predicted from Sr/Ca of fossil corals are usually higher than from other marine proxies. We observed infilling of secondary aragonite, characterised by high Sr/Ca ratios, along intraskeletal pores of a fossil coral from Papua New Guinea that grew during the penultimate deglaciation (130 ± 2 ka). Selective microanalysis of unaltered areas of the fossil coral indicates that SSTs at $\sim$130 ka were $\leq$1°C cooler than at present in contrast with bulk measurements (combining infilled and unaltered areas) which indicate a difference of 6–7°C. The analysis of unaltered areas of fossil skeletons by microprobe techniques may offer a route to more accurate reconstruction of past SSTs. **Citation:** Allison, N., A. A. Finch, A. W. Tudhope, M. Newville, S. R. Sutton, and R. M. Ellam (2005), Reconstruction of deglacial sea surface temperatures in the tropical Pacific from selective analysis of a fossil coral, *Geophys. Res. Lett.*, *32*, L17609, doi:10.1029/2005GL023183.

1. Introduction

[2] Global climate is strongly influenced by the SSTs of the tropical oceans and ocean-atmosphere interactions in the equatorial Pacific Ocean may play a key role in driving glacial–interglacial cycles [*Pierrehumbert*, 2000]. Accurate reconstruction of the past SSTs of these areas is fundamental for understanding past and future climate variations. The aragonite skeletons of massive corals record environmental information at the time of their deposition and act as archives of past climates. Aragonite Sr/Ca and temperature are inversely related [*Kinsman and Holland*, 1969] and coral Sr/Ca ratios can be used to estimate past SSTs [e.g., *Beck et al.*, 1997]. However, SST estimates from coral Sr/Ca conflict with other proxies in the tropical oceans e.g. Western Pacific corals indicate that SSTs during the most recent [*Beck et al.*, 1997] and penultimate [*McCulloch et al.*, 1999] deglaciations were $\geq$6°C cooler than at present but foraminifera geochemistry indicates glacial-interglacial temperature differences of 3–4°C [*Lea et al.*, 2000; *Visser et al.*, 2003].

[3] In this paper we present a study of the distribution and speciation of Sr in relation to skeletal fabric in a pair of modern and fossil (130 ± 2 ka) corals from Papua New Guinea. These corals were used previously to estimate SSTs [*McCulloch et al.*, 1999] and ENSO variability [*Tudhope et al.*, 2001] during the penultimate deglaciation.

2. Materials and Methods

[4] The corals were collected from uplifted coral terraces at Huon Peninsula [*McCulloch et al.*, 1999]. Both corals appear pristine in hand specimen and X-ray diffraction (XRD) showed no evidence for calcite. We used thermal ionisation mass spectrometry (TIMS [*Tudhope et al.*, 2001]) to analyse the Sr/Ca composition of the bulk skeletons at 1 mm resolution and identify short sections of both corals that were representative of the original published data [*McCulloch et al.*, 1999].

[5] We made polished thin sections from parallel transects of the skeletons, cut perpendicular to the growth surface of the coral skeleton i.e. spanning annual bands and along the axis of maximum linear extension rate. We used Secondary Ion Mass Spectrometry (SIMS; see *Allison and Finch* [2004] for analytical details) with an analytical diameter of $\sim$10 μm to determine the Sr/Ca of different features in each coral. We performed analyses across 15 mm lengths corresponding to 1–2 years growth in each coral. During each analysis the primary beam sputtered the sample to a depth of $\sim$2 μm. External reproducibility (the precision of ten analyses on the standard, calculated as $t^*(s/(\sqrt{10}))$ was typically 0.3%. Sr/Ca precision for a single analysis of 10 cycles was typically 0.5%. The relative ion yield of Sr to Ca was estimated after multiple analyses on the standard OKA carbonatite (Sr/Ca = 13.66 ± 2.02 mmol mol^{-1}, from 3 independent measurements). Fasciculi make up >95% of the skeleton and the mean Sr/Ca of the fasciculi in the modern coral (8.77 mmol mol^{-1}) was comparable (within standardisation error) to the TIMS measurement (8.85 mmol mol^{-1}). To ensure that our TIMS and SIMS data are comparable we have standardised all our SIMS data to this bulk value.

[6] We used Sr K-edge Micro Extended X-ray Absorption Fine Structure (EXAFS) to investigate mineralogy and to determine Sr co-ordination in key areas of each coral. MicroEXAFS were collected on line ID-13, Advanced Photon Source, USA. The monochromatic x-ray beam was scanned across the absorption edge between 16.08 and 16.40 keV at 1.5 eV intervals. Residence times increased with x-ray energy from 1 to 4 s per cycle, resulting

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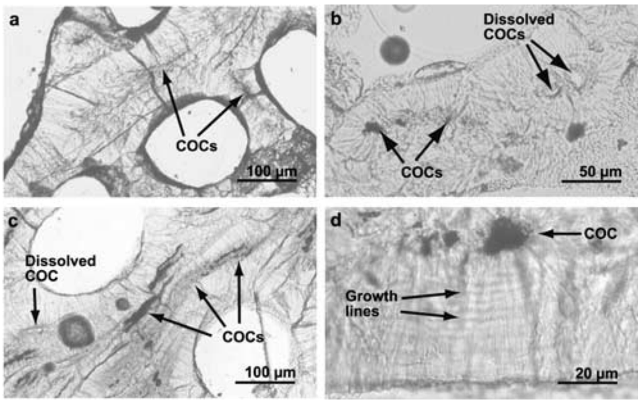

Figure 1. Transmitted light micrographs of the modern (A) and fossil (B, C, D) coral skeletons. Centres of calcification (COCs) are marked on each image.

in EXAFS that maintain their signal-to-noise ratio at higher k. Each spectrum is the sum of 3 scans. Refinements were carried out within a k-range of 2 to 10 and a R range of 1.6 to 4.5 Å. Thermal vibration parameters were set to values of an aragonite standard and co-ordination number (N) was refined [*Allison et al.*, 2005]. The full refinements, including fits of both k^3 $\chi(k)$ and FT k^3 $\chi(k)$ are presented as supplementary data[1].

3. Results and Discussion

[7] Petrographic examination indicated that the fossil coral is subtly altered (Figure 1). Coral skeletons are composed of two key features: centres of calcification (COCs), composed of granular submicron crystals, and fasciculi, composed of bundles of larger acicular crystals which make up the bulk of the coral skeleton [*Cohen et al.*, 2001]. In the modern coral, centres of calcification are typical [*Wainwright*, 1964], appearing as fine dark lines with diameters of 5–10 µm (Figure 1a). In the fossil coral some centres of calcification have dissolved, leaving voids in the section (Figure 1b) but most appear opaque with diameters of up to 20 µm (Figures 1b–1d), indicating some alteration. The opacity may reflect minute intercrystalline pores which provide significant scattering of light [*James*, 1974]. Growth lines, which may record successive positions of the secretory ectoderm [*Cuif et al.*, 1999], are visible in both corals, suggesting the fasciculi are unaltered (Figure 1d).

[8] The spatial resolution of SIMS allows the independent analysis of pristine coral aragonite in diagenetically altered fossil specimens [*Cohen and Hart*, 2004]. We analysed Sr/Ca variations across the fasciculi and centres of calcification in both corals (Figure 2). Corals exhibit Sr/Ca heterogeneity at high spatial resolution that is not temperature dependent [*Meibom et al.*, 2003]. Credible SST trends can be resolved by smoothing data with a ~2 monthly running mean [*Allison and Finch*, 2004] and seasonal Sr/Ca trends by smoothed SIMS and TIMS in the modern coral are in good agreement (Figure 3). However confidence limits on the smoothed SIMS 2 month means are relatively large (they are averages of 17 analyses) and the seasonal SST signal is not significant at the 0.05 level. Mean Sr/Ca of the fasciculi of the modern and fossil corals are 8.85 ± 0.03 (95% confidence limits, n = 129) and 8.92 ± 0.03 mmol mol^{-1} (n = 168) respectively. Mean Sr/Ca of the centres of calcification are 9.18 (±0.05) and 10.21 (±0.08) mmol mol^{-1} respectively. The magnitude of Sr enrichment (14%) in the centres of calcification, compared to the fasciculi, of the fossil coral is much greater than that observed for this and other modern *Porites* corals ([*Allison and Finch*, 2004] ~4%).

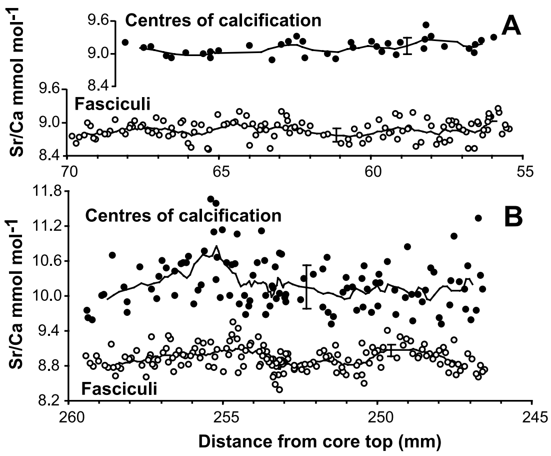

Figure 2. SIMS Sr/Ca records across fasciculi and centres of calcification in the (A) modern and (B) fossil corals. Points indicate single analyses and lines indicate 2 monthly running means. Typical 95% confidence limits of the means were 0.9% for fasciculi of both corals and 1.6 and 3.6% for centres of calcification in the modern and fossil corals respectively.

[9] We performed microEXAFS analyses on centres of calcification in the modern and fossil corals. Both analyses conform to a simplified aragonite structural model [*Finch et al.*, 2003] with closeness of fits equivalent to those of single-phase standards (Table 1). Interatomic distances (R_1) associated with first (Sr-O) shell lie within the range of aragonite distances, but are too long for calcite and the third shell parameters R_3 and PERCA1 [*Finch et al.*, 2003] indicate that Sr is ideally substituted within aragonite in

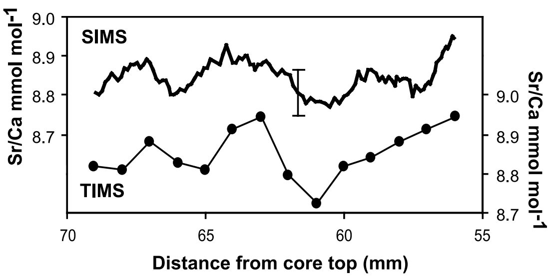

Figure 3. SIMS (fasciculi 2 month running mean with typical 95% confidence limit) and TIMS (2 point i.e. 2 month running mean) trends across the modern coral. TIMS 95% confidence limits (~0.05%) are smaller than the symbols.

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL023183.

Table 1. Refinement Parameters of MicroEXAFS Analyses on Centres of Calcification of Each Coral[a]

Parameter	Modern Coral	Fossil Coral	Aragonite	Calcite	Strontianite
E_f	−9.12 ± 0.29	−8.16 ± 0.44			
R_1 (Å)	2.562 ± 0.005	2.547 ± 0.007	2.416–2.654	2.359	2.567–2.732
R_2 (Å)	2.887 ± 0.020	2.897 ± 0.031	2.905–3.412	3.212	3.031–3.548
R_3 (Å)	4.010 ± 0.012	4.000 ± 0.018	3.893–4.107	4.048	4.106–4.249
PERCA1 (%)	126 ± 18	100 ± 18	100	100	0
R	27.6 %	35.8 %			

[a]The refined values are: Ef (edge energy), R_{1-3} (interatomic distances for the first three shells) and PERCA1 (the % of Ca on third shell sites). Errors indicate mean displacements in each parameter that cause a 2.5% increase in the fit index. The R factor expresses the goodness of fit. For aragonite, R depends on crystal orientation with respect to the polarised x-ray beam. For aragonite, calcite and strontianite structures see *Jarosch and Heger* [1986], *Maslen et al.* [1995], and *Jarosch and Heger* [1988] respectively.

both corals. In the altered centre of calcification, in the fossil coral, there is no evidence of any other Sr-bearing phase e.g., calcite or strontianite, or of Sr clustering in the third (metal-metal) shell, (expressed as PERCA1 < 100%) which would indicate the onset of diffusion-driven exsolution [*Finch and Allison*, 2003].

[10] The Sr concentration of inorganic aragonite is higher than for coral aragonite formed at the same temperature [*Kinsman*, 1969] and aragonite cements in coral skeletons usually contain higher Sr/Ca than the surrounding primary aragonite [e.g., *Enmar et al.*, 2000; *Muller et al.*, 2001], although significant differences are not always observed [*Bar-Matthews et al.*, 1993]. We conclude that the original centres of calcification in the fossil coral have been replaced by secondary aragonite cement, i.e. through growth of cements in intraskeletal pores that had been enlarged through partial dissolution. Similar cementation has been reported in uplifted Pleistocene corals [*Bar-Matthews et al.*, 1993]. Skeleton dissolution begins at the centre of each trabecula i.e. at the centre of calcification [*James*, 1974], (Figure 1b), possibly because the free energy of formation of Sr-supersaturated aragonites increases with Sr content and the centres of calcification (with their generally elevated initial Sr/Ca) are furthest from the thermodynamic equilibrium state [*Finch and Allison*, 2003]. Although aragonite cements commonly occur as epitaxial overgrowths on coral skeletal walls (i.e. in interskeletal pore spaces) in the marine environment [*Enmar et al.*, 2000; *Muller et al.*, 2001] this mode of diagenesis was not evident in the corals examined here.

[11] We cannot be certain when, or in what environment, the diagenesis occurred. On timescales of $\sim 10^5$ years, it seems unlikely that significant skeletal dissolution would occur in the shallow tropical marine environment [*Moore*, 1989] suggesting that dissolution occurred during subaerial exposure in the vadose zone. Aragonite cements are commonly deposited in the marine or intertidal environment [*Moore*, 1989] and this pattern of diagenesis may have been produced while the reef was located in an intertidal or splash-zone position, during either original tectonic uplift, or subsequent eustatic sea level changes through the last glacial-interglacial cycle.

[12] We point counted the thin sections and estimate that centres of calcification occupy 19% and 4% of the volume of the fossil and modern corals. Using these values and our SIMS data we estimate the Sr/Ca of the bulk fossil skeleton (including fasciculi and altered centres of calcification) as 9.16 mmol mol^{-1} which is in reasonable agreement with the measured TIMS value of 9.28 mmol mol^{-1}. We conclude that diagenesis has significantly increased the Sr/Ca of the altered centres of calcification in the fossil coral and as a consequence, bulk Sr/Ca measurements (which combine both fasciculi and centres of calcification) are significantly higher than measurements of fasciculi alone (Figure 4). Centres of calcification occupy only a small volume of modern coral skeletons and the smaller Sr enrichment in these areas does not significantly increase the Sr/Ca of bulk analyses.

[13] The increase of 0.07 mmol mol^{-1} in the unaltered fasciculi of the fossil compared to the modern coral is equivalent to a temperature decrease of $\sim$1°C on the Sr palaeothermometer for this area [*McCulloch et al.*, 1999]. This is in marked contrast with bulk Sr/Ca analyses in the same corals which indicate increases of 0.35 [*McCulloch et al.*, 1999] and 0.42 ± 0.01 (this study) mmol mol^{-1}, equivalent to $\sim$6–7°C. The interpretation of coral skeletal Sr/Ca is complicated by evidence that seawater Sr/Ca varies over glacial-interglacial periods [*Martin et al.*, 1999] and by the unresolved influence of calcification rate on skeletal Sr/Ca. An increase in seawater Sr/Ca of only $\sim$1% would be sufficient to account for the Sr/Ca increase in the fossil coral and could be interpreted as indicating no significant change in SST in the Western Equatorial Pacific between $\sim$130 ka and the present day. We have observed no significant differences between the Sr/Ca of the fasciculi (or of unaltered centres of calcification) of fast and slowly extending corals sampled by SIMS [*Allison and Finch*, 2004] although other authors have reported higher Sr/Ca in slower growing corals [e.g., *de Villiers et al.*, 1995; *Cohen and Hart*, 2004].

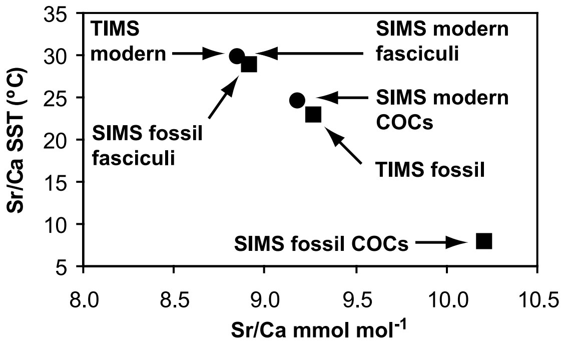

Figure 4. Mean Sr/Ca ratios and estimated SSTs (from the Sr palaeothermometer for the modern coral [4]) for SIMS and TIMS analyses of the modern (circles) and fossil (squares) corals.

The skeletal extension rate of the fossil coral (less than half that of the modern coral) may have biased it towards higher Sr/Ca values.

[14] The original interpretation of the bulk Sr/Ca measurements of the fossil coral was strengthened by $\delta^{18}O$ data which also indicated a large temperature decrease compared to the present day [*McCulloch et al.*, 1999]. However simultaneous diagenetic alteration of Sr/Ca and $\delta^{18}O$ has been observed in recent coral cores [*Muller et al.*, 2001] leading to the reconstruction of the same anomalous temperatures from both proxies.

[15] Our data suggest that SSTs at ~130 ka were $\leq \sim 1°C$ cooler than at present. The brevity of our fossil record (~2 years) may affect our estimate of past mean annual SST. However interannual variations in present mean SST in this region are small (generally <1°C) and the sections of coral core selected for SIMS were representative of the longer sections analysed previously [*McCulloch et al.*, 1999]. Foraminifera Mg/Ca and $\delta^{18}O$ studies indicate that SSTs in the western equatorial Pacific Ocean in marine isotope stage 6 were 3–4°C [*Lea et al.*, 2000; *Visser et al.*, 2003] cooler than at present. Stratigraphic estimates indicate that the fossil coral lived 60–80 m below present day sea level [*McCulloch et al.*, 1999]. In the penultimate deglaciation, ice volume changes in the Pacific lag approximately 2–3 ky behind warming SSTs [*Lea et al.*, 2000; *Visser et al.*, 2003]. This suggests that the coral lived in the mid to late stages of SST warming and our estimate of ~1°C is therefore reasonably consistent with a total glacial-interglacial change of 3°C.

[16] Subtle diagenetic alteration of coral skeletons can significantly increase skeletal Sr/Ca leading to erroneously low estimates of past SST. XRD screening may not detect diagenesis and thorough petrographic examination of fossil corals is recommended. The selective analysis of pristine areas of the skeleton by microprobe techniques may offer a route to more accurate reconstruction of SSTs.

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